

Absorption Spectra Calculation and Charge Distribution Analysis of *para*-azoxyanisole: A Semiempirical Study

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Abstract

Semiempirical study of electronic structure of para-azoxyanisole (PAA) has been carried out. In order to obtain more information on the reactivity of PAA molecule towards nucleophile and electrophile, semiempirical (CNDO/S, and INDO/S) based calculations have been performed to evaluate the negative and positive charge distribution. Further, CNDO/S + CI and INDO/S + CI methods have been employed to calculate and analyze the absorbance spectral measurements in UV-visible range, and charge distribution analysis of the systems. The electronic transitions, absorption wavelength, HOMO (Highest Occupied Molecular Orbital), and LUMO (Lowest Unoccupied Molecular Orbital) energies have been calculated. Further, ultraviolet (UV) stability of the molecule has been discussed. The decreasing order of reactivity of these sites for electrophilic attack, the most, and the lowest negative charge sites may be understood from this analysis.

Keywords: *para-azoxyanisole, oscillator strength, liquid crystal*

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INTRODUCTION

The research involved in the field of liquid crystalline (LC) materials provides a picture of the organization of molecules in molecular level LCs. Consequently, researchers are able to understand how molecules organize themselves in a LC phase [1], and how the interactions with external wavelengths (UV, Visible, IR) lead to specific properties of a LC [2, 3]. The analysis of photo sensitivity to UV light is a striking issue for the manufacture of next generation LC displays. The spontaneous interaction of UV light with LC molecules [4] is a rich field of current scientific inquiry with a wide spectrum of possible applications. Optical features in the ultraviolet-visible (UV-Vis) region can often be traced to the excitation of specific types of electrons in a material.

The simulation results have also been used to provide a computational route to the prediction of some of the key material properties of LCs. These determine how well the LC materials behave in practical applications such as displays and adaptive optics. Usually, this is monitored by UV-Vis spectroscopy at the absorption maxima, which implies a destructive read-out of molecular systems.

Hence, it is necessary to identify the molecular structures that can withstand a longer UV exposure. The chemistry of azoxy-based liquid crystals is characterized by azoxy-group. This group has two nitrogen atoms and an oxygen atom. One of them is doubly bonded with a lone pair of electrons, while the other is doubly bonded that bears a positive charge. In this work, we describe the electronic structures of the above LCs and their reactivity with respect to partial atomic charges [5].

The calculation of absorption spectra is interesting since number of methods have been involved to calculate the molecular vertical excitation energies, absorption wavelength [6], and oscillator strength of electronic transitions [7]. Statistical theories have interpreted these calculations to unequal perturbation of light absorber between the ground and excited state of the molecules. The transition probability for a given excitation is usually characterized by the oscillator strength that is related to the integrated intensity of an absorption band [8]. The macroscopic expression for the extinction coefficient [9] can be deduced from the square of the transition moment on a microscopic level. Most of the methods still stay behind of rather inadequate application for establishing

realistic molecular models. Hence, the alternate use of the semiempirical schemes has an extensive use to calculate absorption spectra as well as electronic transition oscillator strength. Such approaches allow for the calculation of electronic transitions between the ground state and the different excited states, which provides the energies of the corresponding radiations [10].

Molecular structure, and electronic spectral characteristics of PAA molecules using the CNDO/S (complete neglect of differential overlap/ spectroscopy) [11, 12], INDO/S (intermediate neglect of differential overlap/ spectroscopy) [13, 14] schemes have been reported. The HOMO, LUMO energies, absorption wavelength, oscillator strength (f), vertical excitation energies, and dipole moments have been reported. Further, an attempt has been made to explain the UV stability of these systems based on the parameters introduced in this article. An examination of thermodynamic data has revealed that PAA molecule exhibits nematic-isotropic transition temperature at 408 K [15].

METHODOLOGY

The general structural parameters such as bond lengths and bond angles have been taken from the published crystallographic data to construct the electronic structure of the molecule [15]. Using the crystallographic geometry as input, the electronic structure of PAA molecule has been calculated by employing the CNDO/S and INDO/S methods. The configuration interaction (CI) method is widely employed for the calculation of electronic spectra. Using a CI method in combination with a semi-empirical model Hamiltonian, an evaluation of absorption spectra of large organic molecules and LCs becomes possible [16].

The large computational demand associated with the CI calculations places severe limitations on the size of the systems whose excited states can be studied [17]. Hence, we employed the CNDO/S + CI method including all valence electrons, and applied for the calculation of electronic spectra of BCHs molecules. These results have been compared with the INDO/S + CI method. A revised version program of QCPE 174 by Jeff

Reimers, University of Sydney and coworkers has been used for this purpose.

Accurate calculations of molecular vertical excitation energies and the corresponding dipole moments are essential to analyze the electronic absorption spectra. Generating a qualitatively acceptable description of excited states is much more challenging task than the analogous ground-state calculations. This is because, the ground-state electronic wave function is usually well approximated by a single Slater determinant, whereas much more complicated configuration interaction (CI) representations are often needed for the excited states [18]. The electronic structures, excitation energies, and excited state wave functions have been calculated coupled with the configuration interaction (CI) single level of approximation including all $\pi \rightarrow \pi^*$ single excitations. This has been found an adequate to determine the UV-Visible absorption spectra [16] provided that suitable parameterizations are used. In the present work, a comparative analysis has been made by employing the CNDO/S and INDO/S methods to simulate the electronic absorption spectrum.

RESULTS AND DISCUSSION

The electronic structure of PAA molecule has been shown in Figure 1.

Charge Distribution Analysis

The specific charge distributions and electrostatic interactions are probable to play a vital role in LC molecules in the formation of various mesophases. Molecular charge distribution analysis can offer good information about local electrostatic interactions which is not possible from experimental point of view. To parameterize the intermolecular interactions for computer simulation studies atom positioned partial charges are helpful, which are not quantum mechanical observables. It is noticed from Table 1 that even when the magnitude of the partial charge is restrained, it varies very much from atom to atom. These charges represent the electrostatic molecular interactions very well, but they do not show the real charge distribution in the molecule. Due to the shielding of the carbon charges by the adjacent hydrogens, the correct electrostatic potential

might be reproduced by different partial distributions. In spite of these uncertainties, the full set of partial charges is very useful, as it can

provide a detailed insight into the molecular arrangement in mesophases and they reproduce the electrostatic potential very well.

Table 1: Calculated CNDO/S and INDO/S Atomic Net Charges for PAA Molecule.

S. No.	Atom	CNDO/S Charge	INDO/S Charge
1	C	0.01287	0.08063
2	C	0.16019	0.16199
3	C	-0.06035	-0.03583
4	C	0.00737	0.00591
5	C	0.05409	0.05237
6	C	-0.02318	-0.01906
7	C	-0.07754	-0.05257
8	H	0.04921	0.04516
9	H	0.06732	0.05754
10	H	0.13198	0.10163
11	H	0.04616	0.04410
12	H	0.05385	0.03875
13	H	0.05283	0.03672
14	H	0.05266	0.03775
15	N	0.28299	0.36215
16	O	-0.54485	-0.60099
17	O	-0.26560	-0.31624
18	N	0.28299	0.36215
19	C	0.05409	0.05237
20	C	0.00737	0.00591
21	C	-0.06035	-0.03583
22	C	0.16019	0.16199
23	C	-0.07754	-0.05257
24	C	-0.02318	-0.01906
25	H	0.13198	0.10163
26	H	0.04616	0.04410
27	O	-0.26560	-0.31624
28	C	0.01287	0.08063
29	H	0.05385	0.03875
30	H	0.05283	0.03672
31	H	0.05266	0.03775
32	H	0.04921	0.04516
33	H	0.06732	0.05754
34	O	-0.54485	-0.60099

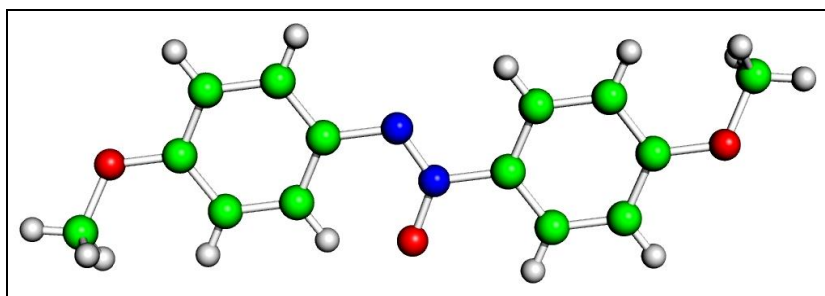


Fig. 1: The Molecular Structure of PAA Molecule.

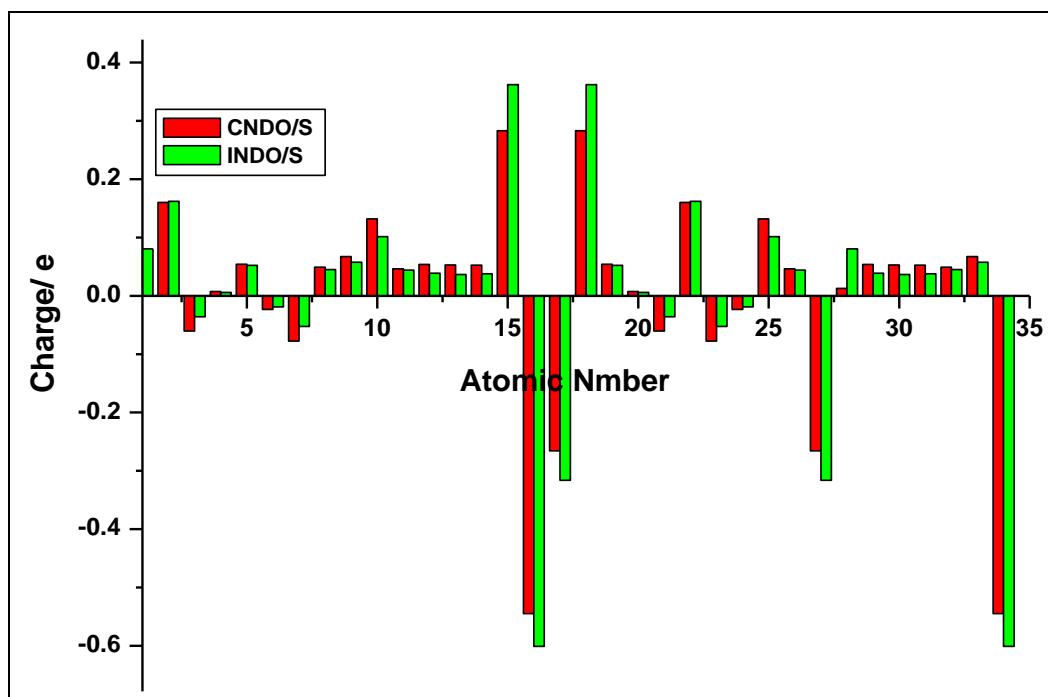


Fig. 2: Charge Distribution Analysis of PAA Molecule Using CNDO/S and INDO/S Method.

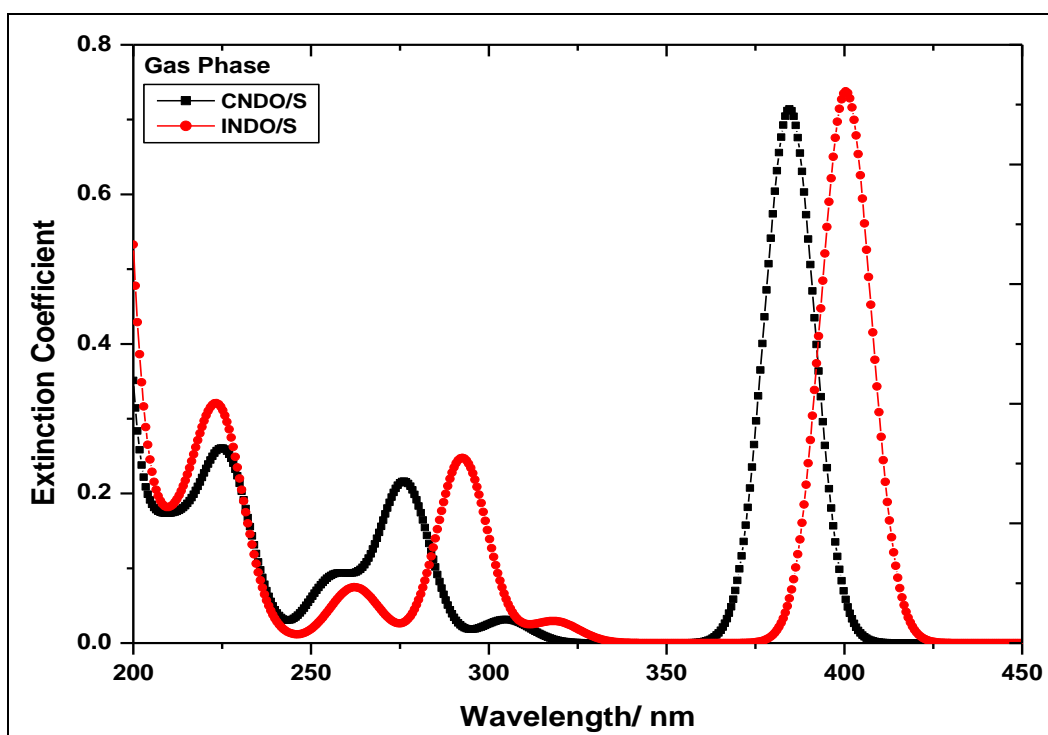


Fig. 3: UV-Visible Absorption Spectra of PAA Molecule using CNDO/S and INDO/S Method.

The charge distribution of PAA molecule based on CNDO/S and INDO/S methods has been shown in Figure 2. The partial atomic charges have been reported in Table 1. CNDO/S data shows that there are twenty four positive charge atoms including two nitrogen, eight carbon atoms, and the other fourteen hydrogen atoms. Thus, there are ten positive

charge sites for nucleophilic attack. The decreasing order of reactivity of these sites for nucleophilic attack is $N_1=N_2$ (0.28299) > $C_2=C_{11}$ (0.16019) > $C_1=C_{14}$ (0.01287) > $C_5=C_8$ (0.05409) > $C_4=C_9$ (0.00737). The most positive positions in PAA are N_1 , and N_2 ($Q_{MAX}=0.28299$), and the lowest positive positions are C_4 , and C_9 ($Q_{MIN}=0.00737$).

Further, INDO/S method also shows the same number of positive charge sites with the same order of atomic sites with the most positive positions N_1 , and N_2 ($Q_{MAX}=0.36215$), and the lowest positive positions are C_4 , and C_9 ($Q_{MIN}=0.00591$).

It has been shown in the Figure 2 that there are ten negative charge sites for electrophilic attack. The decreasing order of reactivity of these sites for electrophilic attack, the most, and the lowest negative charge sites may be understood using the both methods from the Figure 2.

UV-Visible Absorption Spectrum

In any photo induced process the formation of a collective excited state whose properties (energy, and oscillator strength etc.) depend on the structure of constitutive molecules. The UV light causes a gradual degradation of the LC molecules so that the consequent electro-optic effects are altered.

Hence, it is of importance to design the LC material and to explore the structures that can withstand a longer UV exposure. Even a small UV fraction may create major damage in the material via radical formation that triggers photo degradation of the LC materials. This degradation causes deterioration of physical and chemical properties, increasing of conductivity in liquid crystals.

Therefore, UV absorption must be taken into account as a design parameter for material selection from the application point of view. It is expected that the absorption spectrum of a LC molecule containing a single phenyl ring would exhibit similarities to an isolate benzene molecule. The principal absorption bands in the molecules are due to the $\pi \rightarrow \pi^*$ transitions in the benzene analogous part of the molecule.

In general, these benzene-like transitions are roughly conserved in the model systems, but they are influenced by the conjugation length, degree of conjugation, and the different substituents etc. The detailed picture of electronic absorption spectra of PAA molecule based on the semiempirical (CNDO/S, and INDO/S) calculations have been given below

and the electronic spectral data have been reported in Table 2.

The UV-Vis absorption spectrum of PAA molecule is shown in Figure 3 using CNDO/S, and INDO/S methods. It is evident from CNDO/S data that three strong absorptions in the UV region at 224.61 nm, 275.96 nm, and 384.39 nm (λ_{max}) have been observed. However, no absorption has been observed in the visible region. These band arises from the HOMO \rightarrow LUMO transition, and is assigned as $\pi \rightarrow \pi^*$ transition in the molecule. The oscillator strength (f) corresponding to this band at λ_{max} is 0.71.

The INDO/S data shows three strong absorption wavelengths at 223.11 nm, 292.32 nm, and 400.33 nm (λ_{max}). The oscillator strength (f) value corresponding to (λ_{max}) is 0.74, hence showing a good agreement with the CNDO/S method. The corresponding spectral data has been reported in Table 2. Thus, both the semiempirical methods are in very good agreement with each other.

A comparative picture of the vertical excited energy (E_v), oscillator strength (f), and the dipole moment (μ) corresponding to absorption wavelength (λ_{max}) in UV range using the CNDO/S, and INDO/S methods have been reported in Table 2. The HOMO, LUMO and energy gap value have also been reported in Table 2.

The large number of absorption bands in the UV-Visible range causes a higher symmetric representation of PAA molecule. This is because a $\pi \rightarrow \pi^*$ transition is only possible if the direct product of the ground state wave function, the excited one, and the dipole moment operator contains the totally symmetric representation.

More number of $\pi \rightarrow \pi^*$ transitions lead to higher symmetric representation [19] of PAA with respect to the other molecules with less number of $\pi \rightarrow \pi^*$ transitions. Table 3 represents the electrochemical properties PAA molecule. It has been observed that both the methods are in good agreement.

Table 2: The Absorption Bands (AB), Extinction Coefficients (EC), Oscillator Strength (f), Vertical Transition Energy (E_V), HOMO (H), LUMO (L) Energies, and the Band Gap ($E_g = E_L - E_H$) of PAA Molecule using CNDO/S and INDO/S Methods.

Method	Absorption	Bands/ nm	EC*	f	E_V / eV
CNDO/S		224.61	0.26	0.24	5.49
		275.96	0.22	0.21	4.49
		384.39	0.71	0.71	3.22
H = -8.89eV; L = -2.85eV; $E_g = 6.04$ eV					
INDO/S		223.11	0.32	0.29	5.53
		292.32	0.25	0.25	4.24
		400.33	0.74	0.74	3.10
H = -7.86eV; L = -1.99eV; $E_g = 5.87$ eV					

*EC unit: $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

Table 3: Calculated Values of Ionisation Energy $I = (-E_H)$, Electron Affinity $A = (-E_L)$, Electro Negativity $\chi = (I + A)/2$, Chemical Hardness $\eta = (I - A)/2$, Electronic Chemical Potential $\mu = -(I + A)/2$, Electrophilicity Index $\omega = \mu^2/\eta$, and Softness $S = 1/\eta$ of PAA Molecule using CNDO/S, and INDO/S Methods.

Molecule	Method	I/eV	A/eV	χ /eV	η /eV	μ /eV	ω /eV	S/eV ⁻¹
PAA	CNDO/S	8.89	2.85	5.87	3.02	-5.87	11.40	0.33
	INDO/S	7.86	1.99	4.92	2.93	-4.92	8.26	0.34

CONCLUSIONS

A semiempirical approach on absorption spectra calculation and charge distribution analysis leads to the following conclusions:

1. The PAA molecule exhibits three $\pi \rightarrow \pi^*$ transitions in UV range as per the both methods, which represents the higher symmetric representation of the molecule.
2. The charge distribution analysis provides an understanding of possible atomic sites for electrophilic and nucleophilic attacks.
3. The PAA molecule exhibits UV stability up to 384.39 nm, and 400.33 nm as per CNDO/S and INDO/S data. Further, an excellent agreement has been found between the two methods, in estimating most of the spectral parameters.

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